Improving Catalysis with a "Noble" Material

Carbon aerogels are produced in a variety of shapes and sizes. The carbon gives the aerogel its color and makes it electrically conductive.

AEROGELS are an impressive feat of science and technology. These highly porous, low-density, lighter-than-air structures have become exceedingly useful at the Laboratory in laser target fabrication, energetic composites, sensors, ceramics, and coatings. Over the last decade, researchers have tailored the properties of aerogels in an effort to optimize them for different applications. Using a process referred to as doping, they incorporate additional chemical elements into the material. However, this doping process can be challenging because of aerogel's complex pore structure. Recently, a team of Livermore researchers helped develop an efficient method to dope carbon aerogel—an electrically conductive material—with the noble metal platinum. This method could lead to the development of new designer materials for fuel cells, hydrogen storage, and pollution-control technologies.

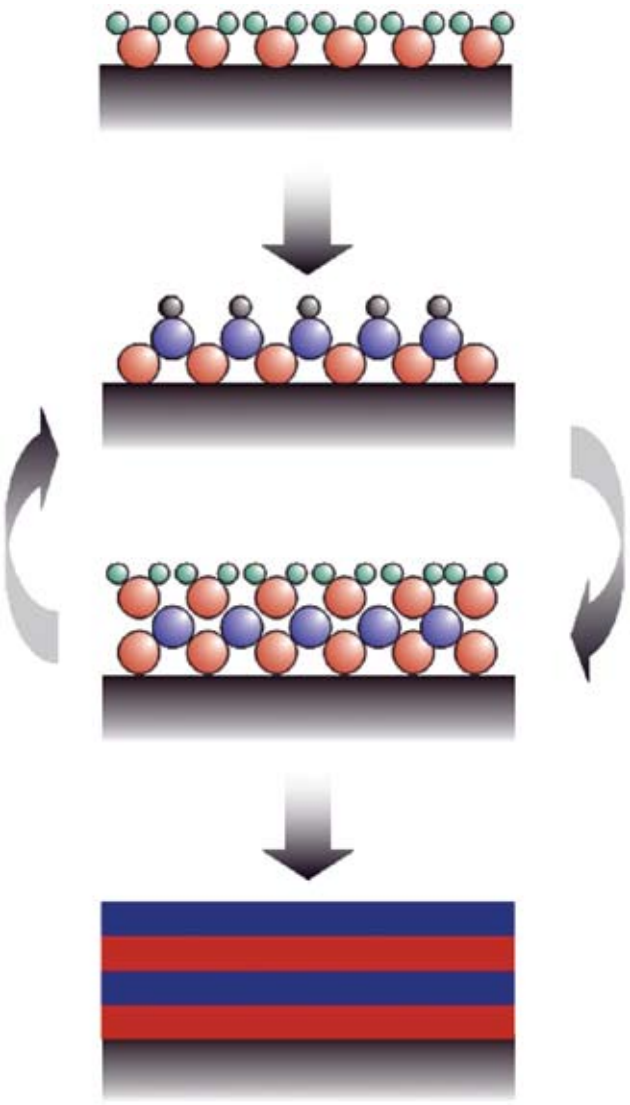
Platinum is an effective catalyst because it can accelerate chemical reactions without being consumed or altered. As an example, catalytic converters on gas-powered vehicles use platinum to convert poisonous carbon monoxide into carbon dioxide through oxidation. In hydrogen fuel cells, platinum is used to catalyze the electrochemical reactions that produce electrical energy. For technologies such as these, more platinum means higher conversion rates. Unfortunately, platinum is expensive, making technologies that require large amounts of the material too costly for everyday applications. However, by incorporating platinum into carbon aerogels, scientists from the Laboratory, Stanford University, and the University of Bremen in Germany have shown that when it comes to platinum, less can do more.

Using atomic layer deposition (ALD)—a gas deposition process that provides atomic-level control of thin films—the team added minute amounts of platinum to uniform discs of carbon aerogel. These platinum-loaded carbon aerogels were then tested for how well they converted carbon monoxide to carbon dioxide. "The catalytic oxidation of carbon monoxide using platinum is fairly well understood and is an easy way to benchmark the material," says Ted Baumann, a chemist in Livermore's Advanced Materials Synthesis Group. The results showed that platinum-loaded carbon aerogels achieved nearly 100 percent conversion efficiency with minimal amounts of platinum, as little as 0.05 milligrams of platinum per square centimeter.

A Complex Kind of Jell-O

Aerogels' internal structure consists of a network of interconnected nanometer-size particles. Because of their structure, aerogels exhibit interesting properties such as low mass densities and large internal surface areas. These properties are a direct result of the methods used to prepare the materials. In a process known as sol-gel chemistry, a solution of reactants is treated to induce the formation of nanometer-size particles, which connect to one another to create a three-dimensional solid network. According to Baumann, who fabricated the carbon aerogels for the experiments, "Making aerogels is a little like making Jell-O." When making Jell-O, gelatin is heated with water and then cooled to create an extremely dilute gelatin network that is responsible for Jell-O's solidlike properties. When making aerogel, the fluid is removed from the pores of the three-dimensional network while the structure remains intact. "The process is equivalent to removing all the water from a Jell-O mold without it collapsing," says Baumann. This transformation requires special drying techniques that typically involve supercritical fluids.

Carbon aerogels, despite their high porosity, can be very strong and are capable of supporting hundreds of times their own weight. Because they are so porous, they also have very high surface areas. For example, the aerogels used in the platinum catalysis experiments have surface areas of approximately 480 square meters per gram. This high surface area allows more of the catalyst to be exposed



In atomic layer deposition (ALD), conformal films are deposited sequentially exposing a substrate surface to two different precursor species whereby surface termination between two states (gray and green circles) is switched. These different surface functionalizations are responsible for the self-limiting character of the ALD process. The process is repeated until the desired thickness is obtained.

when reacting with external chemicals. As a result, less catalyst is needed to produce efficient results.

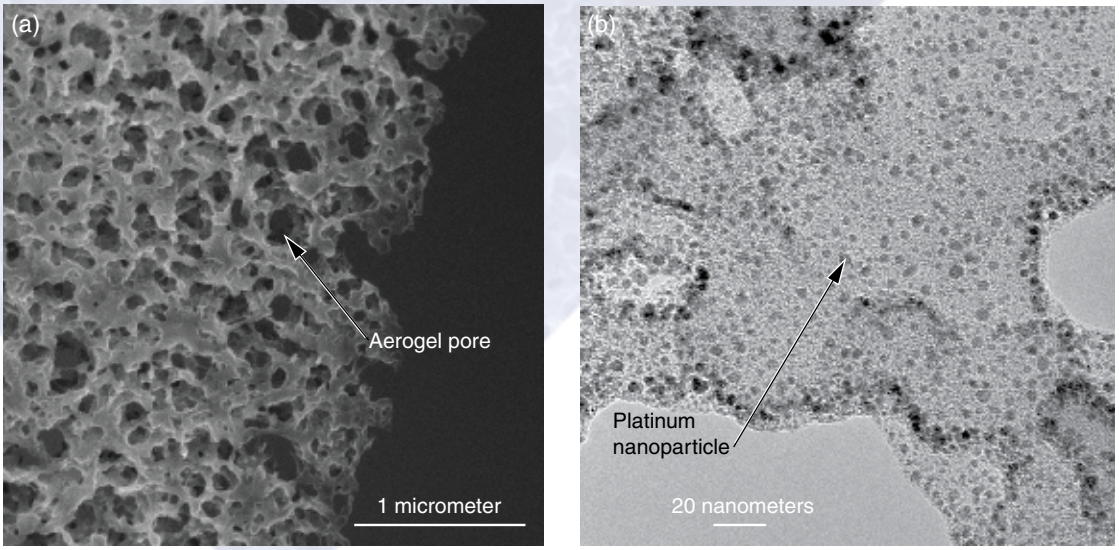
A Successful Sequence

Incorporating catalyst particles into aerogels in a controlled fashion can be challenging because of the material's extremely small pore networks. According to Juergen Biener, a materials scientist in Livermore's Nanoscale Synthesis and Characterization Laboratory who led the project, "Nanoporous materials can be difficult to dope without interfering with their structure. However, the self-limiting character of the ALD process is ideally suited for depositing particles in nanoporous materials with atomic-level control."

In ALD, chemical precursors, or species, in their vapor (gas) form are sequentially pulsed into a reaction chamber containing a sample surface—in the case of the catalysis experiments, a carbon aerogel substrate. Inside the chamber, each species chemisorbs to the sample surface one atom at a time, eventually creating a thin monolayer film. Once the first chemical occupies all available adsorption sites, the surface is passivated, and the film growth stops until the surface is reactivated by exposure to the second gas precursor. Thus, in ALD, film growth is self-limiting, that is, restricted by the number of adsorption sites on the sample surface and the number of reaction cycles.

Baumann says ALD is different from other film-producing techniques, such as chemical vapor deposition, where one or more elements are added to a substrate all at once. Chemical vapor deposition is used in the semiconductor industry to create thin films for transistors. "If we used chemical vapor deposition to coat the inner surfaces of an aerogel, the material being deposited would quickly plug the aerogel's pores, and the coating would not be uniform," says Baumann.

The platinum ALD experiments were conducted at Stanford University in the laboratory of professor Stacey Bent. Uniform disks of carbon aerogel measuring 500 micrometers thick and approximately 1 centimeter wide were placed in a warm-wall chemical reactor heated to 120°C. The team used methylcyclopentadienyl-trimethylplatinum ($MeCpPtMe^3$) and oxygen as the two precursor gases in the experiment. First, $MeCpPtMe^3$ was pulsed into the reactor for 20 minutes, providing ample time for the gas to infuse the aerogel. Then, the reactor was purged with nitrogen for 10 minutes to remove excess precursor molecules remaining in the chamber. Next, oxygen was added for another 10 minutes. The oxygen reacted with the $MeCpPtMe^3$ already on the substrate, transforming the platinum into its solid, metallic state. This step was followed by another 10-minute pulse



(a) A cross-sectional micrograph from a scanning electron microscope shows the high porosity of carbon aerogels. This sample was treated with platinum using ten atomic layer deposition cycles. (b) A higher magnification micrograph from a transmission electron microscope reveals the deposition of platinum nanoparticles with an average size of 2.4 nanometers.

of nitrogen. Because the team wanted to test how little platinum was needed to produce an efficient catalyst, the carbon aerogels were exposed to two, five, and ten deposition cycles for comparison.

Team members Sergei Kucheyev and Morris Wang characterized the ten-cycle platinum-loaded aerogels at Livermore using Rutherford backscattering spectrometry and cross-sectional transmission electron microscopy. The characterization revealed that the deposited platinum does not form a continuous thin film on the surface of the carbon aerogel. Rather, the platinum–aerogel interaction produces hemispherical platinum nanoparticles less than 5 nanometers in diameter. Forming such small platinum nanoparticles is key to a high catalytic efficiency because more of the catalyst's atoms are exposed at the surface, thus increasing the catalyst's ability to induce chemical reactions.

The catalytic properties of the platinum-loaded aerogels were then tested at the University of Bremen. Aerogel substrates exposed to the various deposition cycles were individually placed inside a glass continuous-flow reactor. A combination of nitrogen and oxygen was mixed with carbon monoxide and injected into the reactor. The team compared the conversion rates of each of the aerogels for oxidizing the carbon monoxide into carbon dioxide. Surprisingly, they found the aerogel that had undergone only two ALD cycles had the same conversion efficiency—nearly 100 percent conversion in the 150 to 250°C range—as those that had been through five and ten cycles. In other words, less platinum could be used to obtain the same catalytic effect.

Another "Noble" Cause

Baumann's interest in the platinum catalysis experiments was directly related to his work on a Department of Energy–funded project for hydrogen storage. However, Baumann and Biener have also explored the potential of other nanoporous materials such as gold for use in catalytic and other applications. "As we learn more about the surface chemistry of these materials, we can more fully understand their unique properties," says Biener.

According to these scientists, the potential use for nanoporous materials is virtually untapped. As Baumann, Biener, and other researchers continue their work on nanoporous structures, the scientific and technological innovations they bring about could have a significant effect on the way electric, catalytic, and waste management processes are performed today. In the future, nanoporous materials such as platinum-loaded aerogels could play a key role in applications for water treatment, hydrogen storage technology, and more efficient fuel cells that use less but do more.

—Caryn Meissner

Key Words: atomic layer deposition (ALD), carbon aerogels, catalysis, catalyst, fuel cell, hydrogen storage, nanoporous materials, oxidation, platinum.

For further information contact Juergen Biener (925) 422-9081 (biener2@llnl.gov) or Ted Baumann (925) 423-5543 (baumann2@llnl.gov).